

# **Byproducts of Sulfur Hexafluoride (SF<sub>6</sub>) Use in the Electric Power Industry**

Prepared for

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## Forward

This document provides summary information on sulfur hexafluoride (SF<sub>6</sub>) byproducts. It was prepared for the U.S. Environmental Protection Agency (U.S. EPA), Global Programs Division by ICF Consulting, Inc., under Contract No. 68-W5-0068, Work Assignment No. 0005AA-83. This document was developed as a service to partners of the *SF<sub>6</sub> Emissions Reduction Partnership for Electric Power Systems*. The information presented in this document does not replace existing regulations or guidance regarding these compounds. Rather, this document was designed solely as an overview of the most significant byproducts identified to date. If you have suggestions and/or information that would improve this document, please send them to

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or send an electronic mail to [Blackman.Jerome@epa.gov](mailto:Blackman.Jerome@epa.gov). For more information on the *SF<sub>6</sub> Emissions Reduction Partnership for Electric Power Systems*, see <http://www.epa.gov/highgwp1/sf6/index.html>.

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## 1. Introduction and Background

Sulfur hexafluoride ( $\text{SF}_6$ ) is a relatively nontoxic gas used in a number of applications for its inert qualities. The dielectric and other physical and chemical properties related to its lack of reactivity have led to the extensive use of  $\text{SF}_6$  as an insulating medium in switching equipment (e.g., circuit breakers) by electric utilities. While  $\text{SF}_6$  is inert during normal use, when electrical discharges occur within  $\text{SF}_6$ -filled equipment, toxic byproducts can be produced that pose a threat to health of workers who come into contact with them. This paper discusses these byproducts and how they are formed, and also summarizes relevant health and safety concerns, as well as handling, detection, and safety procedures and guidelines.

U.S. EPA produced this background paper as a service to its partners in the *SF<sub>6</sub> Emission Reduction Partnership for Electric Power Systems*. This is a voluntary program in which partner companies agree to reduce  $\text{SF}_6$  emissions through technically and economically feasible actions.  $\text{SF}_6$  is a potent and persistent greenhouse gas, with a global warming potential approximately 24,000 times greater than carbon dioxide over a 100-year time horizon and a residency in the atmosphere of more than 3,000 years. Although  $\text{SF}_6$  is critical to the reliable distribution of electricity, program participants recognize the importance of careful management and responsible use.

## 2. Formation and Concentrations of $\text{SF}_6$ Byproducts

### *Formation of $\text{SF}_6$ Byproducts*

$\text{SF}_6$  can decompose into byproducts when exposed to four types of electric discharges (CIGRE<sup>1</sup> 1997):

- partial corona discharges caused by insulation defects;
- spark discharges that occur at insulation defects or during switching operations;
- switching arcs that occur in load break switches and power circuit breakers; and
- failure arcs that occur due to insulation breakdown or switchgear interruption failure.

Each discharge can result in different mixtures and concentrations of byproducts.

### *Concentrations of $\text{SF}_6$ Byproducts*

Numerous studies have characterized the byproducts of  $\text{SF}_6$ . Dervos and Vassiliou (2000) have summarized the most important ones (considering toxicity and risk) and the amounts of each formed under conditions similar to those found in gas insulated switchgear (GIS) equipment (see Table 1). These data were obtained by exposing  $\text{SF}_6$  to repeated sparking under experimental conditions, and thus the decomposition products and concentrations formed under actual conditions can vary depending on the equipment used and the type of electrical discharge (CIGRE 1997).

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<sup>1</sup> CIGRE (the International Council on Large Electric Systems) is a permanent non-governmental and non-profit-making international association based in France. This group has established a working group (Study Committee 23) that is focused on concerns related to substations, including  $\text{SF}_6$  and its byproducts. The web site established by Study Committee 23 is located at <http://www.cigre-sc23.org>.

**Table 1. Gaseous SF<sub>6</sub> Decomposition Byproducts  
and Typical Concentrations During Repeated Sparking**

<b>Chemical Formula</b>	<b>Chemical Name</b>	<b>Chemical Abstracts Service Registry Number</b>	<b>Experimental Concentration (percent by volume)<sup>a</sup></b>
HF	Hydrogen fluoride	7664-39-3	1.0
SOF <sub>2</sub> (SF <sub>4</sub> ) <sup>b</sup>	Thionyl sulfide (sulfur tetrafluoride)	7783-42-8 (7783-60-0)	0.5
SOF <sub>4</sub>	Sulfur tetrafluoride oxide	13709-54-1	0.085
SiF <sub>4</sub>	Silicon tetrafluoride	7783-61-1	0.085
S <sub>2</sub> F <sub>10</sub> (SF <sub>5</sub> ) <sup>c</sup>	Disulfur decafluoride	5714-22-7	0.025
SO <sub>2</sub> F <sub>2</sub>	Sulfuryl fluoride	2699-79-8	0.006
SO <sub>2</sub>	Sulfur dioxide	7446-09-5	0.002

Table adapted from Dervos and Vassiliou (2000).

<sup>a</sup> Note that these concentrations represent the measured concentration for the experimental conditions studied. The conditions were designed to simulate a real sparking occurrence; however, actual air concentrations in the vicinity of GIS will vary from these data.

<sup>b</sup> SF<sub>4</sub> is readily hydrolyzed to SOF<sub>2</sub>.

<sup>c</sup> S<sub>2</sub>F<sub>10</sub> is referred to by some authors as sulfur pentafluoride or SF<sub>5</sub>.

Additional byproducts that may be formed through arcing or other electrical discharges include SF<sub>2</sub>, SOF<sub>10</sub>, S<sub>2</sub>O<sub>2</sub>F<sub>10</sub>, and H<sub>2</sub>S, as well as a number of metal fluorides (e.g., copper fluoride (CuF<sub>2</sub>), aluminum fluoride (AlF<sub>3</sub>)) and tungsten compounds (e.g., WF<sub>6</sub>, WO<sub>3</sub>) (CIGRE 1997; U.S. EPA 2001a).

### **3. Health and Safety Concerns**

Information on SF<sub>6</sub> byproducts has improved substantially in recent years. In its 1991 report, CIGRE identified only three gaseous SF<sub>6</sub> byproducts that pose a significant health threat (taking into account reaction quantities and toxicity): SOF<sub>2</sub>, SO<sub>2</sub>, and HF (Mauthe and Pettersson 1991). More recent research has identified S<sub>2</sub>F<sub>10</sub> as the byproduct of greatest concern due to its relatively high toxicity (James et al. 1993; Dervos and Vassiliou 2000), and occupational safety organizations have examined occupational exposures for several additional gaseous SF<sub>6</sub> byproducts.

#### *Human Health Effects*

According to information listed in the Hazardous Substances Databank (HSDB), gaseous SF<sub>6</sub> byproducts such as SF<sub>4</sub>, SiF<sub>4</sub>, SO<sub>2</sub>F<sub>2</sub>, SO<sub>2</sub>, and HF are extremely irritating to the eyes, nose, and throat (NLM 2001). Other human health effects of these gases include pulmonary edema, skin and eye burns, nasal congestion, and bronchitis due to their corrosive characteristics. Solid byproducts such as AlF<sub>3</sub> and CuF<sub>2</sub> dusts are also irritating to exposed skin and eyes, and the nose, throat, and lungs when inhaled (NLM 2001). If copper salts are inhaled in sufficient concentration so that it reaches the gastrointestinal tract (via cough and mucociliary mechanisms), they act as irritants producing salivation, nausea, vomiting, gastric pain, hemorrhagic gastritis, and diarrhea (NLM 2001).

Several incidents involving human exposure to possible SF<sub>6</sub> byproducts have been reported.

- In the U.S., six workers were exposed during repair work on electrical equipment (Kraut and Lilis 1990). The workers experienced symptoms including burning/watering eyes, nasal irritation/epistaxis, throat irritation, chest tightness/wheezing/shortness of breath, coughing (in one case producing blood), nausea/vomiting, fatigue, and headaches. Most symptoms occurred immediately following or up to one week after the exposure event. Some workers' symptoms did not resolve until a month later or (in one case) a year later. No long-term physical effects were observed. Chemical evaluation at the site qualitatively identified the presence of SF<sub>4</sub>.
- In the U.K., two workers collapsed after entering an SF<sub>6</sub> storage tower (James et al. 1993). One of the workers suffered pulmonary edema for the three days following exposure. No long term effects were reported for either worker. Following the incident, both SF<sub>6</sub> and SO<sub>2</sub>F<sub>2</sub> were detected at levels that exceeded occupational exposure limits.
- In the Netherlands in 1989, an accident was reported involving two people who were exposed to unidentified substances resulting from a switchgear equipment failure (Mauthe and Pettersson 1991). The equipment contained SF<sub>6</sub>; upon failure, a small amount of powder was observed (likely solid metal fluorides). Both people recovered within two weeks.
- A case of serious injury was reported to CIGRE in which an electrician repairing a circuit breaker was exposed to SF<sub>6</sub> decomposition products released by the equipment (Mauthe and Pettersson 1991). The worker lost consciousness and then awakened with a burning sensation in his chest. The worker's lung capacity was reduced by 45 percent. (CIGRE reports that had oxygen been administered more quickly, the damage would have been greatly reduced.)
- Several instances of minor skin irritation from exposure to SF<sub>6</sub> decomposition products have been reported to CIGRE (Mauthe and Pettersson 1991).

These instances of human exposure provide useful anecdotal evidence of the possible human health effects due to exposure to SF<sub>6</sub> byproducts, although specific byproduct compounds were not identified in all cases.

#### *Cell and Animal Toxicity Data*

Cell culture toxicity tests have been performed on S<sub>2</sub>F<sub>10</sub> and other SF<sub>6</sub> byproducts (summarized in James et al. 1993). The tests results indicate that S<sub>2</sub>F<sub>10</sub> is more than 43 times more toxic to cell cultures than the other SF<sub>6</sub> byproducts tested (SOF<sub>2</sub>, SF<sub>4</sub>, SOF<sub>4</sub>, SiF<sub>4</sub>, SO<sub>2</sub>F<sub>2</sub>, SO<sub>2</sub>, HF). Additionally, whole animal toxicity studies have further characterized the toxicity of S<sub>2</sub>F<sub>10</sub> and other SF<sub>6</sub> byproducts. A complete summary of these data is beyond the scope of this paper, but specific animal toxicity information for SF<sub>4</sub>, SiF<sub>4</sub>, SO<sub>2</sub>F<sub>2</sub>, SO<sub>2</sub>, HF, AlF<sub>3</sub> can be found in HSDB (NLM 2001). Animal studies indicate that these byproducts are extremely irritating when inhaled. Animals exposed to these gases via inhalation exhibit lung damage (e.g., lung irritation, edema, and hemorrhages) (Dervos and Vassiliou 2000; HSDB 2001).

## 5. Handling, Detection, and Safety Procedures and Guidelines

Numerous guidelines have been published regarding the handling, detection, and safety of SF<sub>6</sub> gas and its byproducts. These guidelines basically specify that employees minimize exposure to SF<sub>6</sub> byproducts by wearing protective equipment when handling and disposing SF<sub>6</sub> byproducts and by meeting specific exposure concentration standards.

### *Handling Procedures and Guidelines*

SF<sub>6</sub> recycling and handling guidelines are described in detail in CIGRE guide number 117 (CIGRE 1997). Procedures specific to individual manufacturers' equipment types are also reported to be available directly from manufacturers. SF<sub>6</sub> handling procedures as provided by utility partners can be found on U.S. EPA's *SF<sub>6</sub> Emissions Reduction Partnership for Electric Power Systems* web page <http://www.epa.gov/highwp1/sf6/> (U.S. EPA 2001a). These guidelines often include procedures for handling hazardous SF<sub>6</sub> byproducts. U.S. EPA has also prepared a catalog that lists guidelines and standards for the handling and management of SF<sub>6</sub> (U.S. EPA 2001b).

### *Detection Procedures and Guidelines*

SF<sub>6</sub> byproducts are difficult to detect chemically under normal working conditions. The presence of various SF<sub>6</sub> electrical discharge decomposition products and impurities (as well as the presence of SF<sub>6</sub> itself) makes measurement of the different byproducts problematic. A recent report in *Transmission and Distribution World* summarized methods that may allow for on-site and field monitoring of SF<sub>6</sub> byproducts with portable instrumentation (Baumbach et al. 2000). The *NIOSH Pocket Guide to Chemical Hazards* (NIOSH 1997) presents measurement methods and signs and symptoms of exposure for S<sub>2</sub>F<sub>10</sub>, SF<sub>4</sub>, SO<sub>2</sub>, HF, and SO<sub>2</sub>F<sub>2</sub>, as well as SF<sub>6</sub>.

SF<sub>6</sub> byproducts such as SOF<sub>3</sub> and SF<sub>4</sub> have a strong irritating "rotten egg" odor at low concentrations, and, at high concentrations, are irritating to the eyes, nose, throat, and lungs (U.S. EPA 2001; NLM 2001). Solid byproducts (i.e., metal fluoride byproducts) are white, gray, or tan powders that often can be observed when present and are irritating to exposed skin (Edison Technical Center 1997; U.S. EPA 2001a; NLM 2001). However, these gross physical indicators of the presence of byproducts should not be relied upon as safety mechanisms due to the possibility of severe injury, especially given that the most toxic byproduct, S<sub>2</sub>F<sub>10</sub>, is generally odorless in pure form at typical environmental temperature.

### *Safety Procedures and Guidelines*

Safety precautions for hazardous SF<sub>6</sub> byproducts are often addressed in SF<sub>6</sub> handling procedures for gas-insulated electrical equipment. (See the electric utility partners' SF<sub>6</sub> handling procedures on U.S. EPA's web page <http://www.epa.gov/highwp1/sf6/> (U.S. EPA 2001a). Also see the U.S. EPA catalog – available from the same web page – of SF<sub>6</sub> guidelines and standards (U.S. EPA 2001b).) Many SF<sub>6</sub> handling procedures require the worker to wear protective clothing and an approved respirator when the presence of decomposition products are suspected (e.g., when the SF<sub>6</sub>-filled breakers are exposed to a severe arc for an abnormal period of time due to improper operation of the breaker). Industrial hygiene practices can be found in the *NIOSH Pocket Guide to Chemical Hazards* (NIOSH 1997), including respirator selections, exposure limits, signs and symptoms of exposure, and procedures for emergency treatment for S<sub>2</sub>F<sub>10</sub>, SF<sub>4</sub>, SO<sub>2</sub>, HF, SO<sub>2</sub>F<sub>2</sub>, fluorides, as well as SF<sub>6</sub>.

Table 2 compiles the available occupational safety standards for the gaseous byproducts identified in Table 1 of this paper. SF<sub>6</sub> is included for reference. Table 3 lists exposure limits for fluorides, aluminum, and copper compound dusts. The parameters presented in Tables 2 and 3 are defined below.

- Permissible exposure limit - ceiling (PEL-ceiling): Defined by the Occupational Safety and Health Administration (OSHA), the PEL-ceiling is a specified concentration of the chemical in air that must not be exceeded during any part of the working exposure for any amount of time.
- Recommended exposure limit - ceiling (REL-ceiling): The REL - ceiling is concentration of the chemical in air that should not be exceeded, as recommended by the National Institute for Occupational Safety and Health (NIOSH).
- Recommended exposure limit - time-weighted average (REL-TWA): The REL-TWA is the time-weighted average concentration for up to a 10-hour workday during a 40-hour workweek that should not be exceeded, as recommended by NIOSH.
- Permissible exposure limit - time-weighted average (PEL-TWA): Defined by OSHA, the PEL-TWA is the time-weighted average concentration that must not be exceeded during any 8-hour work shift of a 40-hour work-week.
- Short-term exposure limit (STEL): Defined by OSHA, the STEL is the concentration that must not be exceeded over a 15-minute period.
- Recommended short-term exposure limit (RSTEL): The RSTEL is a 15-minute time-weighted average concentration that should not be exceeded at any time during a workday, as recommended by NIOSH.
- Level immediately dangerous to life or health (IDLH): Developed by NIOSH, the IDLH is the maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without irreversible health effects (designed to aid in the selection of a respirator only).
- Threshold limit value - ceiling (TLV-C): Established by the American Conference of Governmental Industrial Hygienists (ACGIH), the TLV-C is a specified concentration of the chemical in air that should not be exceeded during any part of the working exposure for any amount of time.
- Threshold limit value - time-weighted average (TLV-TWA): Established by ACGIH, the TLV-TWA is a the time-weighted average concentration that should not be exceeded based on a normal 8 hour work day/40 hour work week.

Occupational exposure limits were not located for some of the SF<sub>6</sub> byproducts (including SOF<sub>4</sub> and SiF<sub>4</sub>). The occupational standards listed in Tables 2 and 3 were developed by occupational health organizations in the United States. CIGRE literature and information in HSDB indicate that international exposure values also exist for some SF<sub>6</sub> byproducts (Mauthe and Pettersson 1991; NLM 2001).

**Table 2. Available Inhalation Exposure Limits for SF<sub>6</sub> and Gaseous Byproducts of SF<sub>6</sub>**

Substance	Parameter	Exposure limit value	Defining organization
S <sub>2</sub> F <sub>10</sub> (SF <sub>5</sub> ) (sulfur decafluoride or pentafluoride)	PEL-TWA	0.025 ppm	OSHA
	PEL-ceiling <sup>a</sup>	0.01 ppm	OSHA
	REL-ceiling	0.01 ppm	NIOSH
	IDLH	1 ppm	NIOSH
	TLV-C	0.01 ppm	ACGIH
SF <sub>4</sub> (sulfur tetrafluoride)	PEL-ceiling <sup>b</sup>	0.1 ppm	OSHA
	REL-ceiling <sup>c</sup>	0.1 ppm	NIOSH
	TLV-C	0.1 ppm	ACGIH
SO <sub>2</sub> (sulfur dioxide)	PEL-TWA <sup>b</sup>	2 ppm	OSHA
	STEL <sup>b</sup>	5 ppm	OSHA
	REL-TWA	2 ppm	NIOSH
	RSTEL	5 ppm	NIOSH
	IDLH	100 ppm	NIOSH
	TLV-TWA	2 ppm	ACGIH
HF (hydrogen fluoride)	PEL-TWA	3 ppm	OSHA
	STEL <sup>b</sup>	6 ppm	OSHA
	REL-ceiling	6 ppm	NIOSH
	REL-TWA	3 ppm	NIOSH
	IDLH	30 ppm	NIOSH
SO <sub>2</sub> F <sub>2</sub> (sulfuryl fluoride)	PEL-TWA	5 ppm	OSHA
	STEL <sup>b</sup>	10 ppm	OSHA
	REL-TWA	5 ppm	NIOSH
	RSTEL	10 ppm	NIOSH
	IDLH	200 ppm	NIOSH
SF <sub>6</sub> (sulfur hexafluoride)	PEL-TWA	1,000 ppm	OSHA
	REL-TWA <sup>c</sup>	1,000 ppm	NIOSH
	TLV-TWA	1,000 ppm	ACGIH

All values listed in this table were cited in ACGIH (1989), James et al. (1993), NIOSH (1997), or OSHA (2000).

ppm = parts per million; ppb = parts per billion; ppm and ppb are given by volume in air.

<sup>a</sup> The PEL-TWA of 0.025 ppm was revised in 1989 to a PEL-ceiling value of 0.01 ppm; however, enforcement of the new limit of 0.01 ppm has been stayed by OSHA, until it publishes a notice in the Federal Register regarding an available sampling and analytical technique.

<sup>b</sup> PEL or STEL was vacated by the U.S. Circuit Court of Appeals on June 30, 1993; however, OSHA may enforce it under the “general duty clause” in Section 5(a)(1) of the Occupational Safety and Health Act. Some states enforce vacated PELs and STELs.

<sup>c</sup> NIOSH has not established an IDLH value for this substance.

**Table 3. Available Inhalation Exposure Limits for Solid Byproducts of SF<sub>6</sub>**

Substance	Parameter	Exposure limit value	Defining organization
Fluorides (measured as fluorine (F))	PEL-TWA	2.5 mg/m <sup>3</sup>	OSHA
	TLV- TWA	2.5 mg/m <sup>3</sup>	ACGIH
Aluminum soluble salts (measured as aluminum (Al))	PEL-TWA <sup>a</sup>	2 mg/m <sup>3</sup>	OSHA
	REL-TWA	2 mg/m <sup>3</sup>	NIOSH
Copper dusts (e.g., CuF <sub>2</sub> )	PEL-TWA	1 mg/m <sup>3</sup>	OSHA
	REL-TWA	1 mg/m <sup>3</sup>	NIOSH
	IDLH	100 mg/m <sup>3</sup>	NIOSH
	TLV-TWA	1 mg/m <sup>3</sup>	ACGIH

All values listed in this table were cited in NLM (2001) and NIOSH (1997)

<sup>a</sup> PEL was vacated by the U.S. Circuit Court of Appeals on June 30, 1993; however, OSHA may enforce it under the “general duty clause” in Section 5(a)(1) of the Occupational Safety and Health Act. Some states enforce vacated PELs.

The Department of Transportation (DOT) provides guidance for emergency response for transportation incidents involving hazardous materials in its *2000 Emergency Response Guidebook*. Health warnings, fire mitigation, evacuation procedures, protective clothing prescriptions, and first aid procedures are available for SO<sub>2</sub>F<sub>2</sub> (DOT no. 2191) in Guide 123 and SF<sub>4</sub> (DOT no. 2418) and HF (DOT no. 1052) in Guide 125 (DOT 2000).

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